Reaction BNXX

k(300)	A	Ea	Notes	
Same k as rxn BRXX			71	BZ(NO2)-O. = NPHE

Notes

71	This is included to avoid problems if these radicals are ever formed under conditions where both HO2 and NO2 are very low (which is considered to be unlikely under most ambient conditions), and can be considered to represent its reaction with organics present. The rate constant is arbitrary, and is such that this process becomes significant only if [NO2] < ~3x10-6 ppm and [HO2] < 1x10-5 ppm.

Explicit and Lumped Molecule Organic Products

Reaction FAHV

	Notes	
Phot Set= HCHO_R	73	HCHO + HV = #2 HO2. + CO

Notes

73	Absorption cross sections and quantum yields recommended by IUPAC (Atkinson et al, 1997a) used. Absorption cross sections used are those given for T = 285K.

This treatment of the radical product producing channel for HCHO photolysis is consistent with present knowledge.

Reaction FAVS

	Notes	
Phot Set= HCHO_M	73	HCHO + HV = H2 + CO

Notes

73	Absorption cross sections and quantum yields recommended by IUPAC (Atkinson et al, 1997a) used. Absorption cross sections used are those given for T = 285K.

This treatment of the molecular product producing channel for HCHO photolysis is consistent with present knowledge.

Reaction FAOH

k(300)	A	Ea	Notes	
9.19e-12	8.60e-12	-0.04	31	HCHO + HO. = HO2. + CO + H2O

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).

The reactants, products and rate parameter are consistent with present knowledge.

Reaction FAH2

k(300)	A	Ea	Notes	
7.79e-14	9.70e-15	-1.24	31	HCHO + HO2. = HOCOO.

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).

The reactants, products and rate parameter are consistent with present knowledge.

Reaction FAHR

k(300)	A	Ea	Notes	
1.76e+2	2.40e+12	13.91	31	HOCOO. = HO2. + HCHO

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).

The reactants, products and rate parameter are consistent with present knowledge.

Reaction FAHN

k(300)	A	Ea	Notes	
Same k as rxn MER1			74	HOCOO. + NO = HCOOH + NO2 + HO2.

Notes

74	Rate constant assumed to be the same as used for methylperoxy + NO.

The reactants and products are consistent with present knowledge. The rate parameter is consistent with the rate parameter used for CH3O2 + NO.

Reaction FAN3

k(300)	A	Ea	Notes	
6.06e-16	2.00e-12	4.83	75	HCHO + NO3 = HNO3 + HO2. + CO

Notes

75	T=298K Rate constant recommended by IUPAC (Atkinson et al, 1979a). Temperature dependence is as estimated by IUPAC (Atkinson et al, 1979a).

The reactants, products and rate parameter are consistent with present knowledge. But the rate parameter is known only within a factor of 2. The rate parameter used is consistent with the more recent recommendation of Atkinson et al. (1999).

Reaction AAOH

k(300)	A	Ea	Notes	
1.57e-11	5.60e-12	-0.62	31	CCHO + HO. = CCO-O2. + H2O

Notes

	Notes	
31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).	

The reactants, products and rate parameter are consistent with present knowledge.

Reaction AAHV

	Notes	
Phot Set= CCHO_R	76	CCHO + HV = CO + HO2. + C-O2.

Notes

76	Absorption cross sections and quantum yields recommended by IUPAC (Atkinson et al, 1997a, 1999) used. Reaction assumed to occur primarily by breaking the C-CHO bond. Pathway forming molecular products from acetaldehyde is calculated to be negligible under atmospheric conditions, and is not included in the model.

This treatment of the radical product producing channel for acetaldehyde photolysis is consistent with present knowledge. Neglect of the molecular product channel is acceptable.

Reaction AAN3

k(300)	A	Ea	Notes	
2.84e-15	1.40e-12	3.70	77	CCHO + NO3 = HNO3 + CCO-O2.

Notes

77	Rate constant expression recommended by IUPAC, Supplement V (Atkinson et al, 1997a).

The reactants, products and rate parameter are consistent with present knowledge. The rate parameter used is consistent with the more recent recommendation of Atkinson et al. (1999).

Reaction PAOH

k(300)	A	Ea	Notes	
2.00e-11	2.00e-11	---	78,31, 79, 80	RCHO + HO. = #.034 RO2-R. + #.001 RO2-N. + #.965 RCO-O2. + #.034 CO + #.034 CCHO + #-0.003 XC

Notes

78	The mechanism for RCHO is based on reactions estimated for propionaldehyde.
31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
79	OH reactions at various positions in the molecule estimated using the group-additivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996).
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter

(1999).	

The reactants, products and rate parameter are consistent with present knowledge. and the assumptions as stated in the notes.

Reaction PAHV

	Notes	
Phot Set= C2CHO	78,76	RCHO + HV = CCHO + RO2-R. + CO + HO2.

Notes

78	The mechanism for RCHO is based on reactions estimated for propionaldehyde.
76	Absorption cross sections and quantum yields recommended by IUPAC (Atkinson et al, 1997a, 1999) used. Reaction assumed to occur primarily by breaking the C-CHO bond. Pathway forming molecular products from acetaldehyde is calculated to be negligible under atmospheric conditions, and is not included in the model.

Note 76 is not correct for Reaction PAHV because it discusses acetaldehyde and not propionaldehyde. Otherwise the reaction appears to be consistent with present knowledge.

Reaction PAN3

k(300)	A	Ea	Notes	
Same k as rxn AAN3			78,81	RCHO + NO3 = HNO3 + RCO-O2.

Notes

78	The mechanism for RCHO is based on reactions estimated for propionaldehyde.
81	Assumed to have same rate constant and analogous mechanism as reaction of acetaldehyde.

This procedure may underestimate the rate parameter for this reaction. Figure 2 suggests that there is a roughly log-linear relationship between k_{HO} and k_{NO3} for HCHO and CH3CHO. If the most recent values for k_{HO} and k_{NO3} for HCHO and CH3CHO are fit we get $k_{NO3} = 2.78*k_{HO} + 15.44$. This yields a k_{NO3} of 5.0E-15 for propionaldehyde if a k_{HO} of 2.0E-11for propionaldehyde is assumed.

Reaction K3OH

k(300)	A	Ea	Notes	
1.94e-13	1.10e-12	1.03	31,82	ACET + HO. = HCHO + CCO-O2. + R2O2.

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
82	Reaction in the presence of NOx is assumed to involve formation of CH3C(O)CH2O., after one NO to NO2 conversion. Based on the data of Jenkin et al (1993), this radical is

	believed to rapidly decompose to HCHO + CH3CO.

The reactants, products and rate parameter are consistent with present knowledge.

Reaction K3HV

	Notes	
Phot Set= ACETONE	83	ACET + HV = CCO-O2. + C-O2.

Notes

83	Absorption cross sections and quantum yields used are those recommended by IUPAC (Atkinson et al, 1997a) except as noted. The reported quantum yields at 230 and 330 are expected to be high and an estimated correction was made as discussed by Carter et al (1993b). The corrected quantum yield data for wavelengths less than 290 nm were then fit to a smooth curve to estimate the quantum yields for higher wavelengths, with no weight being given to the highly uncertain 330 nm point. As discussed by Carter et al (1993b), using these corrections results in better fits of model calculations to environmental chamber experiments involving acetone.

The reactants and products are consistent with present knowledge. This approach to the treatment of the photolysis rates appears to be reasonable.

Reaction K4OH

k(300)	A	Ea	B	Notes	
1.20e-12	1.30e-12	0.05	2.0	31, 79, 80	MEK + HO. = #.37 RO2-R. + #.042 RO2-N. + #.616 R2O2. + #.492 CCO-O2. + #.096 RCO-O2. + #.115 HCHO + #.482 CCHO + #.37 RCHO + #.287 XC

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
79	OH reactions at various positions in the molecule estimated using the group-additivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996).
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).

The rate parameter is in agreement with the recommendations of Atkinson et al. (1999). The estimation procedure used is reasonable and the sum of the rate parameters for the HO reactions at various positions in the molecule sum to within 13% of the measured rate parameter.

Reaction K4HV

	Notes	
Phot Set= KETONE qy= 1.0e-1	84	MEK + HV = CCO-O2. + CCHO + RO2-R.

Notes

84	The absorption coefficients used for MEK are from Moortgat (Private communication, 1996). The overall MEK quantum yield of 0.1 was derived from fits to UNC chamber data as determined by Carter et al (1986), and is consistent with results of MEK reactivity experiments carried out in our laboratories (Carter et al, 1999a). The reaction is assumed to proceed primarily by breaking the weakest CO-C bond.

The absorption coefficients for MEK from Moortgat are the best available. The quantum yield must be regarded as uncertain since it is derived from environmental chamber data and is not the result of a direct measurement. The assumed mechanism is reasonable.

Reaction MeOH

k(300)	A	Ea	B	Notes	
9.34e-13	3.10e-12	0.72	2.0	85	MEOH + HO. = HCHO + HO2.

Notes

85	The mechanism and rate constants are as recommended by IUPAC (Atkinson et al, 1997a, 1999). The branching ratio is for T=298K only. The overall reaction assumes the major fate of the alpha hydorxy radical is reaction with O2 to form HO2 and HCHO.

The reactants and the rate parameter are in agreement with the Atkinson et al. (1999) recommendations. The CH2OH reaction channel does represent 85% of the overall reaction at 298K. The products are reasonable if the CH2OH produced mainly reacts through abstraction of the H atom attached to the OH group. The CH3O reaction channel would be expected to produce almost all HCHO and HO2.

Reaction MER9

k(300)	A	Ea	Notes	
5.46e-12	2.90e-12	-0.38	86	COOH + HO. = H2O + #.35 {HCHO + HO.} + #.65 C-O2.

Notes

86	Rate constant and branching ratio for initial OH reaction based on IUPAC (Atkinson et al, 1997a, 1999) recommendation. The .CH2OOH radical is assumed to rapidly decompose to HCHO + OH, based on its high estimated exothermicity.

The reactants, products and rate parameters are consistent with the recommendations of Atkinson et al. (1999).

Reaction MERA

	Notes	
Phot Set= COOH	87	COOH + HV = HCHO + HO2. + HO.

Notes

87	Absorption cross sections from IUPAC (Atkinson et al, 1997a, 1999), which also recommends assuming unit total quantum yield, but gives no recommendation as to the exact mechanism. Breaking the O-O bond assumed to be the major pathway.

The reactants, products, quantum yields and absorption cross sections are consistent with current knowledge.

Reaction LPR9

k(300)	A	Ea	Notes	
1.10e-11	1.10e-11	--	88,89	ROOH + HO. = H2O + RCHO + #.34 RO2-R. + #.66 HO.

Notes

88	The mechanism for ROOH is based on reactions estimated for n-propyl hydroperoxide.
89	Reaction at the OOH position is assumed to be as fast as in CH3OOH. Reaction at the 1-position is estimated to be ~7x10-12 (i.e., ~2/3 of the time) based on comparing rates of analogous reactions for methanol, ethanol, and CH3OOH (IUPAC, 1997a, 1999). The alpha-hydroperoxy radicals are assumed to decompose rapidly to OH and the carbonyl on the basis of estimated high exothermicity. Reaction at the 2- or 3-positions are estimated to occur no more than ~10% of the time and are neglected.

The basis of this reaction appears to be highly uncertain but the estimation procedures used for the products and rate parameter are reasonable.

Reaction LPRA

	Notes	
Phot Set= COOH	90	ROOH + HV = RCHO + HO2. + HO.

Notes

90	Reaction assumed to occur with the same rate and analogous mechanism as methyl hydroperoxide.

The reactants, products, quantum yields and absorption cross sections are consistent with current knowledge but the reaction is uncertain due to that fact that it is derived through analogy.

Reaction GLHV

	Notes	
Phot Set= GLY_R	91,92	GLY + HV = #2 {CO + HO2.}

Notes

91	Absorption cross sections from Plum et al (1983), as recommended by IUPAC (Atkinson et al, 1997a, 1999) in the case of glyoxal.
92	For the low wavelength band, a constant quantum yield of 0.4 is assumed, based on data of Langford and Moore (1984). For the high wavelength band, quantum yield is assumed to decrease linearly to zero at the threshold wavelength of 418 nm, starting at a "falloff" wavelength, which is adjusted to yield fits to chamber data for acetylene - NOx and acetylene reactivity experiments, as discussed by Carter et al (1997c). "Best fit" falloff wavelength of 380 nm used. Note that this gives overall quantum yields which are ~1.4 times higher than overall quantum yield reported by Plum et al (1983) for conditions of those experiments. Although use of acetylene reactivity data is a highly indirect way to obtain glyoxal quantum yields, it is considered to be a less uncertain way to estimate radical quantum yields then the data of Plum et al (1993), which uses a UV-poor light source and only measures rates of glyoxal decay.

The reactants, products, quantum yields and absorption cross sections are consistent with present knowledge but derived photolysis frequencies are uncertain due to the fitting of environmental chamber data.

Reaction GLVM

	Notes	
Phot Set= GLY_ABS qy= 6.0e-3	91,93	GLY + HV = HCHO + CO

Notes

91	Absorption cross sections from Plum et al (1983), as recommended by IUPAC (Atkinson et al, 1997a, 1999) in the case of glyoxal.
93	Plum et al (1983) observed 13% formaldehyde yield in photodecomposition, so overall quantum yield adjusted to give this yield relative to the radical forming process for the spectral distribution of those experiments. A wavelength-independent quantum yield is used because of lack of information on wavelength dependence.

The reactants, products, quantum yields and absorption cross sections are consistent with present knowledge. The use of a wavelength-independent quantum yield contributes to the uncertainty in the derived photolysis frequencies.

Reaction GLOH

k(300)	A	Ea	Notes	
1.10e-11	1.10e-11		31,94, 95	GLY + HO. = #.63 HO2. + #1.26 CO + #.37 RCO-O2. + #-.37 XC

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
94	Product distribution based on the data of Niki et al (1985), as discussed by IUPAC (Atkinson et al, 1997a). Product distribution is calculated for 1 atm air at 298K.
95	HCO(CO)OO. is represented by the lumped higher acyl peroxy species RCO-OO.

The reactants, products and rate parameters are consistent with the recommendations of Atkinson et al. (1999).

Reaction GLN3

k(300)	A	Ea	Notes	
Same k as rxn AAN3			95,96	GLY + NO3 = HNO3 + #.63 HO2. + #1.26 CO + #.37 RCO-O2. + #-.37 XC

Notes

95	HCO(CO)OO. is represented by the lumped higher acyl peroxy species RCO-OO.
96	Assumed to have the same rate constant and mechanism as the analogous reaction with acetaldehyde.

The products are consistent with the treatment of the HO reaction, Reaction GLOH. The rate parameter is uncertain due to its derivation by analogy.

Reaction MGHV

	Notes	
Phot Set= MGLY_ADJ	97	MGLY + HV = HO2. + CO + CCO-O2.

Notes

97	Absorption cross sections obtained from Moortgat (personal communication, 1996). These are essentially the same as those recommended by IUPAC (Atkinson et al, 1997a, 1999), except slightly better resolution. Photolysis at the low wavelength band is assumed to have unit quantum yields, based on data for biacetyl. Photolysis above the cutoff wavelength of 421 nm (Atkinson et al, 1977a) is assumed to have zero quantum yields. For the rest of the high wavelength region, the wavelength dependence was derived by assuming the quantum yields decline linearly from 1 at 344 nm to 0 at a wavelength (407 nm) which was adjusted to be such that the calculated overall quantum yields for the conditions of the experiments of Plum et al (1983) agreed with the overall quantum yield they observed experimentally. The quantum yields recommended by IUPAC (Atkinson et al, 1999) lack sufficient wavelength resolution to be useful for modeling.

The absorption coefficients for MEK from Moortgat are the best available. The procedure used to derive the quantum yields from the experimental data is to be reasonable.

Reaction MGOH

k(300)	A	Ea	Notes	
1.50e-11	1.50e-11	--	31	MGLY + HO. = CO + CCO-O2.

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).

The reactants, products and rate parameters are consistent with current knowledge.

Reaction MGN3

k(300)	A	Ea	Notes	
Same k as rxn AAN3			96	MGLY + NO3 = HNO3 + CO + CCO-O2.

Notes

96	Assumed to have the same rate constant and mechanism as the analogous reaction with acetaldehyde.

The products are consistent with the treatment of the HO reaction, Reaction MGOH. The rate parameter is uncertain due to its derivation by analogy.

Reaction BAHV

	Notes	
Phot Set= BACL_ADJ	91,98	BACL + HV = #2 CCO-O2.

Notes

91	Absorption cross sections from Plum et al (1983), as recommended by IUPAC (Atkinson et al, 1997a, 1999) in the case of glyoxal.
98	Assumed to have unit quantum yield at low wavelength band based on data cited by Atkinson (1994). For the high wavelength band, the quantum yields were assumed to decline linearly from 1 at 350 nm to 0 at a wavelength (420 nm) which was adjusted to be such that the calculated overall quantum yields for the conditions of the experiments of Plum et al (1983) agreed with the overall quantum yield they observed experimentally.

The absorption coefficients for biacetyl are based on glyoxal while the quantum yields are estimated. Given the lack of measurements the procedure is reasonable but the uncertainty in the photolysis frequencies derived from the absorption coefficients and quantum yields are high.

Reaction PHOH

k(300)	A	Ea	Notes	
2.63e-11	2.63e-11	--	99,100	PHEN + HO. = #.24 BZ-O. + #.76 RO2-R. + #.23 GLY + #4.1 XC

Notes

99	Rate constant recommended by Atkinson (1994).
100	The parameterized mechanism is estimated by analogy to the parameterized mechanism derived for cresols (see footnotes for OH + cresol reaction).

The rate parameter is consistent with the recommendations of Atkinson (1994). The uncertainty in the products is relatively high due to the need to fit environmental chamber data.

Reaction PHN3

k(300)	A	Ea	Notes	
3.78e-12	3.78e-12	--	99,101	PHEN + NO3 = HNO3 + BZ-O.

Notes

99	Rate constant recommended by Atkinson (1994).
101	In absence of definitive data concerning this reaction, the same mechanism is used as assumed by Carter (1990). However, see footnotes concerning phenoxy reactions.

The rate parameter is consistent with the recommendations of Atkinson (1994). The reactants and products are consistent with the stated assumptions in the footnotes concerning phenoxy reactions.

Reaction CROH

k(300)	A	Ea	Notes

4.20e-11	4.20e-11	--	99,102	CRES + HO. = #.24 BZ-O. + #.76 RO2-R.
				+ #.23 MGLY + #4.87 XC

Notes

99	Rate constant recommended by Atkinson (1994).
102	The parameterized mechanism is based on that used by Carter (1990), but was reoptimized to fit the NO, ozone, PAN, and cresol data in the o-cresol - NOx experiment EC281.

The rate parameter is consistent with the recommendations of Atkinson (1994) but it should be noted that o-cresol is assumed here. The uncertainty in the products is relatively high due to the need to fit environmental chamber data.

Reaction CRN3

k(300)	A	Ea	Notes	
1.37e-11	1.37e-11		99,101	CRES + NO3 = HNO3 + BZ-O. + XC

Notes

99	Rate constant recommended by Atkinson (1994).
101	In absence of definitive data concerning this reaction, the same mechanism is used as assumed by Carter (1990). However, see footnotes concerning phenoxy reactions.

The rate parameter is consistent with the recommendations of Atkinson (1994) but it should be noted that o-cresol is assumed here. The reactants and products are consistent with the stated assumptions in the footnotes concerning phenoxy reactions.

Reaction NPN3

k(300)	A	Ea	Notes	
Same k as rxn PHN3			103	NPHE + NO3 = HNO3 + BZ(NO2)-O.

Notes

103	Assumed to have the same rate constant as the reaction of NO3 with phenol. Reaction with NO3 is assumed to dominate over reaction with OH radicals and other loss processes.

The assumed rate parameter and products are reasonable although the uncertainty is high due to the lack of measurements.

Reaction BZOH

k(300)	A	Ea	Notes	
1.29e-11	1.29e-11		99	BALD + HO. = BZCO-O2.

Notes

99	Rate constant recommended by Atkinson (1994).

The rate parameter is consistent with the recommendations of Atkinson (1994).

Reaction BZHV

	Notes	
Phot Set= BZCHO qy= 5.0e-2	104	BALD + HV = #7 XC

Notes

104	Absorption coefficients are from Majer et al (1969). The overall quantum yield derived by Carter (1990), which are based on model simulations of benzaldehyde decay rates in SAPRC evacuable chamber experiments, is used. Because of lack of data, the quantum yield is assumed to be independent of wavelength. The products formed from benzaldehyde photolysis are unknown, except that both radical formation and benzene formation appear to be minor (Carter, 1990). This benzaldehyde photolysis mechanism gives reasonably good model simulations of benzaldehyde - NOx experiments recently carried out in the CE-CERT xenon Teflon chamber (Carter et al, 1998a).

Reaction BZNT

k(300)	A	Ea	Notes	
2.73e-15	1.40e-12	3.72	105	BALD + NO3 = HNO3 + BZCO-O2.

Notes

105	T=298K rate constant recommended by Atkinson (1994). Temperature dependence estimated by assuming the reaction has the same A factor as the reaction of NO3 with acetaldehyde.

The rate parameter for 298K recommended by Atkinson, 2.6e-15 cm^3 molecule^{-1} s^{-1}, is consistent with this assignment. The temperature dependence used is highly uncertain due to its reliance on the highly uncertain temperature dependence of the NO3 + NO2 = N2O5 equilibrium constant.

Reaction MAOH

k(300)	A	Ea	Notes	
3.35e-11	1.86e-11	-0.35	106, 80,107	METHACRO + HO. = #.5 RO2-R. + #.416 CO + #.084 HCHO + #.416 MEK + #.084 MGLY + #.5 MA-RCO3. + #-0.416 XC

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).
107	MEK is used to represent hydroxyacetone.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction MAO3

k(300)	A	Ea	Notes	
1.19e-18	1.36e-15	4.20	106, 108, 109, 110	METHACRO + O3 = #.008 HO2. + #.1 RO2-R. + #.208 HO. + #.1 RCO-O2. + #.45 CO + #.117 CO2 + #.2 HCHO + #.9 MGLY + #.333 HCOOH + #-0.1 XC

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
108	The excited HCHO2 biradical is assumed to react as recommended by Atkinson (1997) based on data for the O3 + ethene system, i.e., 37% stabilization, 12% decomposition to HCO + OH, 13% decomposition to CO2 + H2, and 38% decomposition to CO + H2O. Note that this is different than used for this species when formed in the isoprene products mechanisms of Carter and Atkinson (1996) and Carter (1996).
109	The vibrationally excited HCOC(CH3)CO2 biradicals are assumed to rearrange and decompose to HCOC(O)CH2. + OH, where the former forms HCOC(O). + HCHO after O2 addition and NO to NO2 conversion. RCO-O2. is used to represent HCOC(O)OO. in this reaction. Vibrationally excited CH3C(O)CHO2 is assumed to rapidly convert to HCOC(CH3)CO2 as discussed by Carter and Atkinson (1996).
110	The organic acid(s) formed in this reaction represent the formation of stabilized Crigiee biradicals, which are assumed to be consumed primarily by reaction with H2O forming the corresponding acid.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction MAN3

k(300)	A	Ea	Notes	
4.76e-15	1.50e-12	3.43	106, 111, 80,112	METHACRO + NO3 = #.5 {HNO3 + RO2-R. + CO +MA-RCO3.} + #1.5 XC + #.5 XN

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
111	NO3 radical addition assumed to occur primarily at the least substituted position.
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).
112	The product CH3C(O)CH2ONO2 is expected to be relatively unreactive and is represented as "lost nitrogen" + 3 "lost carbons".

The reactants, products and rate parameter are consistent with current knowledge.

Reaction MAOP

k(300)	A	Ea	Notes	
6.34e-12	6.34e-12	--	113,5	METHACRO + O3P = RCHO + XC

Notes

113	Rate constant estimated from linear correlation between log k for OH and O3P reaction. Chamber data for C3+ alkenes are better fit by models assuming O3P reactions with C3+ species do not form radicals. Stable products represented by the lumped higher aldehyde or ketone, depending on type of product(s) expected to be formed.
5	This reaction is probably not important in air, but is included to increase range of applicability.

The reactants, products and rate parameter are estimated and therefore have a high degree of uncertainty. The reaction is probably not important in air under most conditions.

Reaction MAHV

	Notes

Phot Set= ACROLEIN, qy= 4.1e-3	106,114	METHACRO + HV = #.34 HO2. + #.33 RO2-R. + #.33 HO. + #.67 CCO-O2. + #.67 CO + #.67 HCHO + #.33 MA-RCO3. + #-0 XC

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
114	The overall quantum yield was reoptomized to fit the same data as discussed by Carter and Atkinson (1996). In the case of methacrolein, he changes to the other portion of the mechanism resulted in an ~14% increase in the best fit overall quantum yield compared to that derived by Carter and Atkinson (1996). In the case of MVK, the best fit overall quantum yield decreased by a factor of 5.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction MVOH

k(300)	A	Ea	Notes	
1.87e-11	4.14e-12	-0.90	106,80	MVK + HO. = #.3 RO2-R. + #.025 RO2-N. + #.675 R2O2. + #.675 CCO-O2. + #.3 HCHO + #.675 RCHO + #.3 MGLY + #-0.725 XC

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).

The reactants, products and rate parameter are consistent with current knowledge.

Reaction MVO3

k(300)	A	Ea	Notes	
4.74e-18	7.51e-16	3.02	106, 108, 109, 80, 110	MVK + O3 = #.064 HO2. + #.05 RO2-R. + #.164 HO. + #.05 RCO-O2. + #.475 CO + #.124 CO2 + #.1 HCHO + #.95 MGLY + #.351 HCOOH + #-0.05 XC

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
108	The excited HCHO2 biradical is assumed to react as recommended by Atkinson (1997) based on data for the O3 + ethene system, i.e., 37% stabilization, 12% decomposition to HCO + OH, 13% decomposition to CO2 + H2, and 38% decomposition to CO + H2O. Note that this is different than used for this species when formed in the isoprene products mechanisms of Carter and Atkinson (1996) and Carter (1996).
109	The vibrationally excited HCOC(CH3)CO2 biradicals are assumed to rearrange and decompose to HCOC(O)CH2. + OH, where the former forms HCOC(O). + HCHO after O2 addition and NO to NO2 conversion. RCO-O2. is used to represent HCOC(O)OO. in this reaction. Vibrationally excited CH3C(O)CHO2 is assumed to rapidly convert to HCOC(CH3)CO2 as discussed by Carter and Atkinson (1996).
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).
110	The organic acid(s) formed in this reaction represent the formation of stabilized Crigiee biradicals, which are assumed to be consumed primarily by reaction with H2O forming the corresponding acid.

The reactants, products and rate parameter are consistent with current knowledge but there is considerable uncertainty regarding the any potential reaction of Crigiee intermediates with H2O.

Reaction MVN3

k(300)	A	Ea	Notes	
(Slow)			106	MVK + NO3 = #4 XC + XN

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.

It seems surprising that the rate parameter for the reaction of MVK with NO3 is negligible.

Reaction MVOP

k(300)	A	Ea	Notes

4.32e-12	4.32e-12		113,5	MVK + O3P = #.45 RCHO + #.55 MEK + #.45 XC

Notes

113	Rate constant estimated from linear correlation between log k for OH and O3P reaction. Chamber data for C3+ alkenes are better fit by models assuming O3P reactions with C3+ species do not form radicals. Stable products represented by the lumped higher aldehyde or ketone, depending on type of product(s) expected to be formed.
5	This reaction is probably not important in air, but is included to increase range of applicability.

The reactants, products and rate parameter are estimated and therefore have a high degree of uncertainty. The reaction is probably not important in air under most conditions.

Reaction MVHV

	Notes	
Phot Set= ACROLEIN qy= 2.1e-3	106,114, 115	MVK + HV = #.3 C-O2. + #.7 CO + #.7 PROD2 + #.3 MA-RCO3. + #-2.4 XC

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
114	The overall quantum yield was reoptomized to fit the same data as discussed by Carter and Atkinson (1996). In the case of methacrolein, he changes to the other portion of the mechanism resulted in an ~14% increase in the best fit overall quantum yield compared to that derived by Carter and Atkinson (1996). In the case of MVK, the best fit overall quantum yield decreased by a factor of 5.
115	CH2=CHC(O)OO. Is represented by MA-RCO3.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction IPOH

k(300)	A	Ea	Notes	
6.19e-11	6.19e-11		116, 106, 80	ISOPROD + HO. = #.705 RO2-R. + #.006 RO2-N. + #.0 R2O2. + #.289 MA-RCO3. + #.357 CO + #.056 HCHO + #.134 CCHO + #.015 RCHO + #.158 MEK + #.352 PROD2 + #.158 GLY + #.179 MGLY + #-0.514 XC

Notes

116	As discussed by Carter (1996), isoprod is the "four product" lumped isoprene product species whose mechanism is derived by lumping rate constant and product parameters for a mixture of 30% hydroxymethacrolein, and 70% equal amounts of cis and trans HCOC(CH3)=CHCH2OH and HCOCH=C(CH3)CH2OH. These proportions are based on the estimated yields of these products in the reactions of OH with isoprene (Carter and Atkinson, 1996), which are represented by ISOPROD in the four product condensed mechanism (Carter, 1996). The other footnotes refer to the estimated mechanisms for these four individual compounds which were used to derive the lumped ISOPROD mechanism. RCHO, PROD2, MA-RCO3, etc. are used to represent various compounds as indicated in the descriptions of these lumped model species. See Carter and Atkinson (1996) for the specific compounds which can be formed in the various reactions of these species.
106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).

The reactants, products and rate parameter are consistent with current knowledge.

Reaction IPO3

k(300)	A	Ea	Notes	
4.18e-18	4.18e-18		116, 106, 80, 117, 109, 118, 110	ISOPROD + O3 = #.4 HO2. + #.048 RO2-R. + #.048 RCO-O2. + #.285 HO. + #.498 CO + #.14 CO2 + #.125 HCHO + #.047 CCHO + #.21 MEK + #.023 GLY + #.742 MGLY + #.1 HCOOH + #.372 RCO-OH + #-.33 XC

Notes

116	As discussed by Carter (1996), isoprod is the "four product" lumped isoprene product species whose mechanism is derived by lumping rate constant and product parameters for a mixture of 30% hydroxymethacrolein, and 70% equal amounts of cis and trans HCOC(CH3)=CHCH2OH and HCOCH=C(CH3)CH2OH. These proportions are based on the estimated yields of these products in the reactions of OH with isoprene (Carter and Atkinson, 1996), which are represented by ISOPROD in the four product condensed mechanism (Carter, 1996). The other footnotes refer to the estimated mechanisms for these four individual compounds which were used to derive the lumped ISOPROD mechanism. RCHO, PROD2, MA-RCO3, etc. are used to represent various compounds as indicated in the descriptions of these lumped model species. See Carter and Atkinson (1996) for the specific compounds which can be formed in the various reactions of these species.
106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).
117	The HC(O)CHO2 biradical can decopose either to OH + HCO + CO via an internal H abstraction from HCO, or to HCO + HCO2 via rearrangement to HCOCH(O.)O. and decomposition. (The HCO would form HO2 + CO and the HCO2 would form HO2 + CO2 after reaction with O2.) These two pathways are assumed to have equal probability. Note that decomposition for these biradicals is assumed to be faster than for biradicals such as CH3CHO2 because of the weaker H-CO and C-CO bonds.
109	The vibrationally excited HCOC(CH3)CO2 biradicals are assumed to rearrange and decompose to HCOC(O)CH2. + OH, where the former forms HCOC(O). + HCHO after O2 addition and NO to NO2 conversion. RCO-O2. is used to represent HCOC(O)OO. in this reaction. Vibrationally excited CH3C(O)CHO2 is assumed to rapidly convert to HCOC(CH3)CO2 as discussed by Carter and Atkinson (1996).

118	The excited CH3C(O2)CH2OH biradical is assumed to react primarily via rearrangement to the unsaturated hydroperoxide followed by decomposition to OH radicals and the corresponding carbonyl compound, as is assumed in the general alkene mechanism (Carter, 1999b). Two possible such rearrangements can occur in the case of this biradical, one to CH2=C(OOH)CH2OH, which decomposes to OH + HOCH2C(O)CH2., and the other to HOCH=C(OOH)CH3, which decomposes to OH + CH3C(O)CH(.)OH. The relative importances of the competing rearrangements in such cases is estimated by assuming they are approximately proportional to the estimated OH abstracting rate constant from the H-donating group (Carter, 1999b). Based on this, the overall reaction is estimated to be OH + 0.04 HOCH2C(O)CH2. + 0.96 CH3C(O)CH(.)OH, with the subsequent reactions of these radicals being derived by the general estimation methods (Carter, 1999a).
110	The organic acid(s) formed in this reaction represent the formation of stabilizied Crigiee biradicals, which are assumed to be consumed primairly by reaction with H2O forming the corresponding acid.

The reactants, products and rate parameter are consistent with current knowledge but there is considerable uncertainty regarding the any potential reaction of Crigiee intermediates with H2O.

Reaction IPN3

k(300)	A	Ea	Notes	
1.00e-13	1.00e-13		116, 106, 80	ISOPROD + NO3 = #.85 RO2-R. + #.15 MA-RCO3. + #.609 CO + #.15 HNO3 + #.241 HCHO + #.233 RCHO + #.008 MGLY + #.609 RNO3 + #.241 XN + #-.827 XC

Notes

116	As discussed by Carter (1996), isoprod is the "four product" lumped isoprene product species whose mechanism is derived by lumping rate constant and product parameters for a mixture of 30% hydroxymethacrolein, and 70% equal amounts of cis and trans HCOC(CH3)=CHCH2OH and HCOCH=C(CH3)CH2OH. These proportions are based on the estimated yields of these products in the reactions of OH with isoprene (Carter and Atkinson, 1996), which are represented by ISOPROD in the four product condensed mechanism (Carter, 1996). The other footnotes refer to the estimated mechanisms for these four individual compounds which were used to derive the lumped ISOPROD mechanism. RCHO, PROD2, MA-RCO3, etc. are used to represent various compounds as indicated in the descriptions of these lumped model species. See Carter and Atkinson (1996) for the specific compounds which can be formed in the various reactions of these species.
106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).

The reactants, products and rate parameter are consistent with current knowledge.

Reaction IPHV

	Notes	
Phot Set= ACROLEIN qy= 4.1e-3	116,106, 80,119	ISOPROD + HV = #1.233 HO2. + #.467 CCO-O2. + #.3 RCO-O2. + #1.233 CO + #.3 HCHO + #.467 CCHO + #.233 MEK + #-.233 XC

Notes

116	As discussed by Carter (1996), isoprod is the "four product" lumped isoprene product species whose mechanism is derived by lumping rate constant and product parameters for a mixture of 30% hydroxymethacrolein, and 70% equal amounts of cis and trans HCOC(CH3)=CHCH2OH and HCOCH=C(CH3)CH2OH. These proportions are based on the estimated yields of these products in the reactions of OH with isoprene (Carter and Atkinson, 1996), which are represented by ISOPROD in the four product condensed mechanism (Carter, 1996). The other footnotes refer to the estimated mechanisms for these four individual compounds which were used to derive the lumped ISOPROD mechanism. RCHO, PROD2, MA-RCO3, etc. are used to represent various compounds as indicated in the descriptions of these lumped model species. See Carter and Atkinson (1996) for the specific compounds which can be formed in the various reactions of these

species.

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).
119	All the species represented by ISOPROD are assumed to have the same overall photolysis rate as used for methacrolein.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction K6OH

k(300)	A	Ea	Notes	
1.60e-11	1.60e-11	--	120	PROD2 + HO. = #.373 HO2. + #.479 RO2-R. + #.068 RO2-N. + #.028 CCO-O2. + #.052 RCO-O2. + #.218 HCHO + #.083 CCHO + #.555 RCHO + #.122 MEK + #.329 PROD2 + #.872 XC

Notes

120	The PROD2 mechanism was derived by averaging mechanisms for CH3C(O)CH2CH2CH2OH, CH3C(O)CH2CH(CH3)CH2OH, CH3CH(OH)CH2CH2C(O)CH2CH3, CH3CH2CH(OH)CH2CH2C(O)CH2CH3, and CH3CH2CH2CH(OH)CH2CH2C(O)CH2CH3, which were taken as representative of the products formed from VOCs measured in ambient air that are represented by PROD2 in the model (Carter, 1999). The mechanisms for these five representative PROD2 compounds were derived using the mechanism generation and estimation methods discussed by Carter (1999).

The reactants, products and rate parameter are consistent with current knowledge.

Reaction K6HV

	Notes	
Phot Set= KETONE qy= 1.0e-1	120,121	PROD2 + HV = #.968 RO2-R. + #.032 RO2-N. + #.708 R2O2. + #.4 CCO-O2. + #.6 RCO-O2. + #.331 HCHO + #.233 CCHO + #.878 RCHO + #-.221 XC

Notes

120	The PROD2 mechanism was derived by averaging mechanisms for CH3C(O)CH2CH2CH2OH, CH3C(O)CH2CH(CH3)CH2OH, CH3CH(OH)CH2CH2C(O)CH2CH3, CH3CH2CH(OH)CH2CH2C(O)CH2CH3, and CH3CH2CH2CH(OH)CH2CH2C(O)CH2CH3, which were taken as representative of the products formed from VOCs measured in ambient air that are represented by PROD2 in the model (Carter, 1999). The mechanisms for these five representative PROD2 compounds were derived using the mechanism generation and estimation methods discussed by Carter (1999).
121	Assumed to photolyze with the same rate absorption cross section and quantum yields as used for MEK.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction RNOH

k(300)	A	Ea	Notes	
8.50e-12	8.50e-12		122	RNO3 + HO. = #.309 NO2 + #.076 HO2. + #.426 RO2-R. + #.19 RO2-N. + #.639 R2O2. + #.026 HCHO + #.146 CCHO + #.393 RCHO + #.032 ACET + #.143 MEK + #.138 PROD2 + #.218 RNO3 + #.473 XN + #.559 XC

Notes

122	The RNO3 mechanism was derived by averaging mechanisms for CH3CH2CH2CH2CH(ONO2)CH2OH, CH3CH(CH3)CH2C(CH3)(ONO2)CH2CH3, and CH3CH2CH(ONO2)CH2CH2CH2CH3, which were taken as representative of the products formed from VOCs measured in ambient air that are represented by RNO3 in the model (Carter, 1999). The mechanisms for these three representative RNO3 compounds were derived using the mechanism generation and estimation methods discussed by Carter (1999).

The reactants, products and rate parameter are consistent with current knowledge.

Reaction RNHV

	Notes	
Phot Set= IC3ONO2	122,123	RNO3 + HV = NO2 + #.263 HO2. + #.641 RO2-R. + #.096 RO2-N. + #.192 R2O2. + #.392 HCHO + #.085 CCHO + #.403 RCHO + #.052 ACET + #.143 MEK + #.445 PROD2 + #.251 XC

Notes

122	The RNO3 mechanism was derived by averaging mechanisms for CH3CH2CH2CH2CH(ONO2)CH2OH, CH3CH(CH3)CH2C(CH3)(ONO2)CH2CH3, and CH3CH2CH(ONO2)CH2CH2CH2CH3, which were taken as representative of the products formed from VOCs measured in ambient air that are represented by RNO3 in the model (Carter, 1999). The mechanisms for these three representative RNO3 compounds were derived using the mechanism generation and estimation methods discussed by Carter (1999).
123	Absorption cross sections given by IUPAC (Atkinson et al, 1997a, 1999) for isopropyl nitrate are used. As discussed by IUPAC (Atkinson et al, 1999), the quantum yield is expected to be near unity for formation of NO2.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction D1OH

k(300)	A	Ea	Notes

5.00e-11	5.00e-11	--	124, 125	DCB1 + HO. = RCHO + RO2-R. + CO

Notes

124	DCB1 is used to represent aromatic ring fragmentation products that do not undergo significant photodecomposition to radicals. Its mechanism is largely parameterized, but it is based roughly on that expected for unsaturated dicarbonys such as 2-butene-1,3-dial.
125	The rate constant is based on data of Bierbach et al (1994). The reaction is assumed to proceed via addition of OH to double bond, followed by decomposition of the alkoxy radical to HCO and HC(O)CH(OH)CHO, where the latter is represented by RCHO. Although this mechanism may not be what one would estimate for the non-photoreactive unsaturated diketones (Bierback et al, 1994; Tuazon et al, ??) expected to be formed from o-substitued aromatics, best fits to the o-xylene and 1,2,4-trimethylbenzene chamber data are obtained if this mechanism is used.

The rate parameter of Bierbach et al (1994) does include a temperature dependence of k = 2.8e-11*exp(175/T). This might be included in the mechanism.

Reaction D1HV

k(300)	A	Ea	Notes	
(Slow)		--	124, 126	DCB1 + HV = HO2. + #2 CO + RO2-R. + GLY + R2O2.

Notes

124	DCB1 is used to represent aromatic ring fragmentation products that do not undergo signficant photodecomposition to radicals. Its mechanism is largely parameterized, but it is based roughly on that expected for unsaturated dicarbonys such as 2-butene-1,3-dial.
126	The photolysis action spectra of these products are assumed to be similar to that for acrolein, so the absorption cross sections of acrolein are used, with a wavelength-independent overall quantum yield. The overall quantum yield is adjusted to optimize fits of model simulations to the benzene - NOx experiments used in the optimization of the previous version of the mechanism by Carter et al (1997a), The photolyisis mechanism is represented as being similar to that used for DCB2 and DCB3. However, best fits to benzene - NOx experiments are obtained if this photolysis is assumed to be slow, so the reaction is not included in the mechanism.

The reactants, products and rate parameter are consistent with current knowledge but the reaction is uncertain due to the fitting of environmental chamber data.

Reaction D1O3

k(300)	A	Ea	Notes	
2.00e-18	2.00e-18	--	124, 127, 117	DCB1 + O3 = #1.5 HO2. + #.5 HO. + #1.5 CO + #.5 CO2 + GLY

Notes

124	DCB1 is used to represent aromatic ring fragmentation products that do not undergo signficant photodecomposition to radicals. Its mechanism is largely parameterized, but it is based roughly on that expected for unsaturated dicarbonys such as 2-butene-1,3-dial.
127	The rate constant is based on the data of Bierbach et al (1994). The reaction is assumed to involve initial formation of glyoxal and HC(O)CHO2.
117	The HC(O)CHO2 biradical can decopose either to OH + HCO + CO via an internal H abstraction from HCO, or to HCO + HCO2 via rearrangement to HCOCH(O.)O. and decomposition. (The HCO would form HO2 + CO and the HCO2 would form HO2 + CO2 after reaction with O2.) These two pathways are assumed to have equal probability. Note that decomposition for these biradicals is assumed to be faster than for biradicals such as CH3CHO2 because of the weaker H-CO and C-CO bonds.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction D2OH

k(300)	A	Ea	Notes	
5.00e-11	5.00e-11	--	128, 129	DCB2 + HO. = R2O2. + RCHO + CCO-O2.

Notes

128	DCB2 and DCB3 represent the highly photoreactive unsaturated dicarbonyl product formed from the ring-opening reactions of the alkylbenzenes. To fit chamber data using differing light sources, they are represented by two species, which differ only in their action spectra and overall quantum yields, with the action spectrum of DCB2 being like methyl glyoxal, and that of DCB3 being like acrolein, and with the overall quantum yields adjusted separately to fit chamber data. Its reactions are based roughly on estimated reactions of a 5-carbon compound with general structure XC(O)CX=CXC(O)X, where X can be H or alkyl.
129	Assumed to have the same rate constant as used for DCB1. Mechanism represented as OH adding to double bond in XC(O)CX=CXC(O)X, with alkoxy radical decomposing to CH3CO. and XCO-CH(OH)-CXO, the latter being represented by RCHO. Note that the general alkoxy radical estimation method (Carter, 1999) predicts that alkoxy radicals like RCH(OH)CH(O.)C(O)R' will decompose primarily to RCH(OH)CHO + RC(O).

The rate parameter of Bierbach et al (1994) does include a temperature dependence of k = 2.8e-11*exp(175/T). This might be included in the mechanism.

Reaction D2HV

	Notes	
Phot Set= MGLY_ABS qy= 3.7e-1	128,130	DCB2 + HV = RO2-R. + #.5 {CCO-O2. + HO2.} + CO + R2O2. + #.5 {GLY + MGLY + XC}

Notes

128	DCB2 and DCB3 represent the highly photoreactive unsaturated dicarbonyl product formed from the ring-opening reactions of the alkylbenzenes. To fit chamber data using differing light sources, they are represented by two species, which differ only in their action spectra and overall quantum yields, with the action spectrum of DCB2 being like methyl glyoxal, and that of DCB3 being like acrolein, and with the overall quantum yields adjusted separately to fit chamber data. Its reactions are based roughly on estimated reactions of a 5-carbon compound with general structure XC(O)CX=CXC(O)X, where X can be H or alkyl.
130	The overall quantum yields for DCB2 and DCB3 were optimized to give best fits of model simulations of NO oxidation, O3 formation and xylene consumption in m-xylene - NOx chamber runs with various light sources, and also to mini-surrogate - NOx runs. The DCB2 and DCB3 quantum yields had to be adjusted as well as the yields of these products from m-xylene to best fit the data for the various light sources, and also to fit the results of the mini-surrogate as well as the m-xylene only runs. (For the other aromatics, only the

DCB2 and DCB3 yields are optimized.) The photolysis mechanisms are unknown, and probably highly variable depending on the species involved. For an RC(O)CH=CHC(O)H structure, the most energetically favored initial reaction is formation of R. + HCOCH=CHCO., but assuming that mechanism results in a model that consistently under predicts PAN yields in alkylbenzene - NOx chamber experiments. Therefore, a set of products is assumed to be formed that may result from various different reactions, and give predictions of PAN yields that are more consistent with available chamber data.

The reactants, products and rate parameter are consistent with current knowledge but the reaction is uncertain due to the fitting of environmental chamber data.

Reaction D3OH

k(300)	A	Ea	Notes	
5.00e-11	5.00e-11		128, 129	DCB3 + HO. = R2O2. + RCHO + CCO-O2.

Notes

128	DCB2 and DCB3 represent the highly photoreactive unsaturated dicarbonyl product formed from the ring-opening reactions of the alkylbenzenes. To fit chamber data using differing light sources, they are represented by two species, which differ only in their action spectra and overall quantum yields, with the action spectrum of DCB2 being like methyl glyoxal, and that of DCB3 being like acrolein, and with the overall quantum yields adjusted separately to fit chamber data. Its reactions are based roughly on estimated reactions of a 5-carbon compound with general structure XC(O)CX=CXC(O)X, where X can be H or alkyl.
129	Assumed to have the same rate constant as used for DCB1. Mechanism represented as OH adding to double bond in XC(O)CX=CXC(O)X, with alkoxy radical decomposing to CH3CO. and XCO-CH(OH)-CXO, the latter being represented by RCHO. Note that the general alkoxy radical estimation method (Carter, 1999) predicts that alkoxy radicals like RCH(OH)CH(O.)C(O)R' will decompose primarily to RCH(OH)CHO + RC(O).

The rate parameter of Bierbach et al (1994) does include a temperature dependence of k = 2.8e-11*exp(175/T). This might be included in the mechanism.

Reaction D3HV

	Notes	
Phot Set= ACROLEIN qy= 7.3e+0	128,130	DCB3 + HV = RO2-R. + #.5 {CCO-O2. + HO2.} + CO + R2O2. + #.5 {GLY + MGLY + XC}

Notes

| 130 | methyl glyoxal, and that of DCB3 being like acrolein, and with the overall quantum yields adjusted separately to fit chamber data. Its reactions are based roughly on estimated reactions of a 5-carbon compound with general structure XC(O)CX=CXC(O)X, where X can be H or alkyl.

The overall quantum yields for DCB2 and DCB3 were optimized to give best fits of model simulations of NO oxidation, O3 formation and xylene consumption in m-xylene - NOx chamber runs with various light sources, and also to mini-surrogate - NOx runs. The DCB2 and DCB3 quantum yields had to be adjusted as well as the yields of these products from m-xylene to best fit the data for the various light sources, and also to fit the results of the mini-surrogate as well as the m-xylene only runs. (For the other aromatics, only the DCB2 and DCB3 yields are optimized.) The photolysis mechanisms are unknown, and probably highly variable depending on the species involved. For an RC(O)CH=CHC(O)H structure, the most energetically favored initial reaction is formation of R. + HCOCH=CHCO., but assuming that mechanism results in a model that consistently underpredicts PAN yields in alkylbenzene - NOx chamber experiments. Therefore, a set of products is assumed to be formed that may result from various different reactions, and give predictions of PAN yields that are more consistent with available chamber data. |

The reactants, products and rate parameter are consistent with current knowledge but the reaction is uncertain due to the fitting of environmental chamber data.